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(54) Single-stage reforming of high hydrogen content feeds for production of ammonia syn gas.

(57) The present invention as described in Figure 2 is an improved process for the production of ammonia synthesis gas by steam reforming a desulfurized high-hydrogen content feedstock gas 122 by admixing steam 124 therewith and partially reforming the resulting gas mixture in a tubular heat exchanger 130 containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas 134; recovering a partially reformed gas product 136 from the tubular heat exchanger and secondarily reforming this gas in a secondary reformer 140 in the presence of air, which is introduced to the secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3:1 in the ammonia synthesis gas; and treating the reformed gas 134 in a shift conversion zone (160 + 200) to convert CO catalytically with steam to CO₂ and hydrogen to form a gas which can be treated for removing CO and CO₂ by absorption and methanation to produce the ammonia synthesis gas.

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1 SINGLE-STAGE REFORMING OF HIGH HYDROGEN CONTENT FEEDS
2 FOR PRODUCTION OF AMMONIA SYN GAS

2 FIELD OF THE INVENTION

3 The present invention is directed to an improved
4 process for the production of ammonia synthesis gas, and
5 specifically to an improved process which utilizes a high
6 hydrogen content feedstock gas in a single adiabatic re-
7 forming stage without requiring a primary reforming furnace
8 system as is conventional in present processes.

9 DESCRIPTION OF THE PRIOR ART

10 Generally the manufacture of ammonia consists of
11 preparing an ammonia synthesis gas from three separate
12 process components: a nitrogen source, usually air; steam;
13 and a hydrogen source which is conventionally either coal,
14 petroleum fractions, or natural gases. For example, in the
15 preparation of ammonia synthesis gas from a light hydrocarbon
16 feedstock, which may range from natural gas to naphtha, the
17 hydrocarbon feedstock gas is first purified by removing
18 gaseous contaminants, such as sulfur (which would poison the
19 downstream catalysts) from the feedstock by the catalytic
20 hydrogenation of the sulfur compounds to hydrogen sulfide and
21 adsorption of the hydrogen sulfide over a zinc oxide adsorp-
22 tion medium. Subsequent steam reforming of the contaminant-
23 free gas provides the major portion of the hydrogen required
24 for ammonia synthesis from the hydrocarbons in the gas.
25 Reforming is accomplished by a two-stage process in which a
26 mixture of steam and the purified feed gas are first reformed
27 over catalyst in a primary reformer, followed by treatment in
28 a secondary reformer to which air is introduced, in order to
29 provide the required amount of N₂ for ammonia synthesis.
30 However, reforming also produces carbon oxides. The carbon
31 monoxide in the reformed gas is converted to carbon dioxide
32 and additional hydrogen in a shift conversion step, and the
33 carbon dioxide is removed by subsequent scrubbing. Further
34 treatment of the raw synthesis gas by methanation is con-
35 ventionally used to remove additional amounts of carbon

1 dioxide and remaining carbon monoxide from the hydrogen-rich.
 2 gas, resulting finally in an ammonia synthesis gas contain-
 3 ing approximately three parts of hydrogen and one part of
 4 nitrogen, that is, the 3:1 stoichiometric ratio of hydrogen
 5 to nitrogen in ammonia. The ammonia synthesis gas is then
 6 converted to ammonia by passing the gas over a catalytic
 7 surface based upon metallic iron (conventionally magnetite)
 8 which has been promoted with other metallic oxides, and
 9 allowing the ammonia to be synthesized according to the
 10 following exothermic reaction:



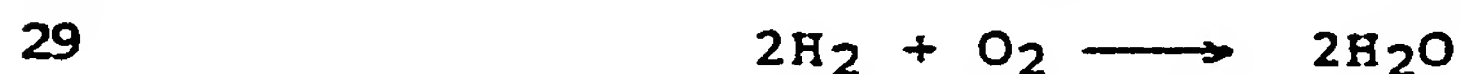
12 The steam reforming of the sulfur-free light hydro-
 13 carbon feedstock is conventionally carried out in a two-stage
 14 process wherein the first stage, that is primary reforming,
 15 produces a partially reformed gas. This partially reformed
 16 gas is introduced along with air into a second stage, that is
 17 secondary reforming, to obtain a greater concentration of
 18 hydrogen and a lesser concentration of hydrocarbons. The
 19 reaction processes occurring in the reforming of the feed-
 20 stock gas begin with the breakdown of hydrocarbons to
 21 methane, carbon dioxide and carbon monoxide:



23 and end with the reforming of these products by the desired
 24 endothermic methane reforming reaction:



26 and by accompanying exothermic reactions:



31 The methane reforming reaction for the production of
 32 hydrogen is highly endothermic and, for feedstocks containing
 33 less than about 80 vol.% H_2 a large heat transfer is
 34 required, which conventionally involves the use of a high
 35 capital investment primary reforming furnace, which also
 36 consumes a significant amount of energy in the form of fuel.
 37 The catalyst for this primary reforming is normally a nickel
 38 catalyst supported on alumina.

1 The subsequent secondary reforming step takes place in
2 a refractory-lined vessel which also contains a nickel
3 catalyst supported on alumina. In conventional steam
4 reforming processes, air is introduced into this adiabatic
5 reforming stage to provide the needed nitrogen for the
6 production of ammonia synthesis gas. Oxygen in the air also
7 reacts with the combustion components in the gas stream
8 coming from the primary reforming stage to increase the
9 temperature and provide heat for this additional reforming of
10 hydrocarbons.

11 U.S. Patent 3,442,613 discloses a two-stage reforming
12 process in which milder primary reforming conditions are
13 employed which results in a larger amount of methane in the
14 primary reformer effluent. Excess air is then fed to the
15 secondary reformer to permit increased exothermic hydrogen
16 combustion therein, which aids in the reforming of the larger
17 methane volumes fed thereto. Thereafter, the excess N₂,
18 introduced via the air feed to the secondary reformer, is
19 removed in a cryogenic separation step.

20 U.S. Patent 3,584,998 relates to a one-stage reforming
21 process in which natural gas, excess air and steam are
22 preheated in heat exchange with reformer effluent gas and
23 then reformed, followed by water gas shift and CO₂ scrubbing
24 treatments and then by a cryogenic process in which excess N₂
25 is removed from the scrubbed reformer effluent gas.

26 U.S. Patent 3,649,558 also relates to a single stage
27 reformer, in which air is introduced in excess amounts to the
28 secondary-type reformer. Excess N₂ is removed in a subsequent
29 cryogenic section.

30 U.S. Patents 4,079,017 and 4,162,290 relate to the use
31 of parallel steam reformers for the primary reforming of the
32 hydrocarbon feed.

33 B. Chatterjee, "Ammonia From Hydrocarbons--An Improved
34 Process", Fertiliser News, pp. 19-22 (December 1980) dis-
35 closes another single-stage reforming process in which
36 oxygen-enriched excess air is combined with natural gas and
37 steam and reacted in an autothermal reformer, followed by
38 shift reactions, boiler feed water heat recovery, CO₂

1 recovery and methanation. Excess methane remains in the
2 reformer effluent gas and is removed in a downstream cryo-
3 genic section, which also serves to separate excess N₂.

4

5

SUMMARY OF THE INVENTION

6 The present invention, is broadly directed to an
7 improved process for the production of ammonia synthesis gas,
8 and specifically to an improved process which utilizes a
9 high-hydrogen content feedstock gas in a single adiabatic
10 reforming stage without requiring a primary reforming furnace
11 system as is conventional in present processes.

12 The improved process of this invention provides an
13 ammonia synthesis gas which, after shift conversion, is
14 characterized by low methane content and does not contain
15 excess nitrogen, and which can therefore be passed directly,
16 after conventional treatment for CO₂ scrubbing and methan-
17 ation, to an ammonia synthesis reactor for formation of
18 ammonia. The process therefore produces an ammonia syn gas
19 stream without the need for use of the expensive cryogenic
20 purification processes required by the prior art, and at the
21 same time avoids the need to use a conventional primary
22 reformer. This results in a large savings in equipment costs
23 and on-going operating expenses.

24 The process of this invention also permits the use of
25 higher process pressures in the reforming section than have
26 heretofore been possible due to pressure design limitations
27 imposed by current primary reformer tubing metallurgy.

28

BRIEF DESCRIPTION OF THE DRAWINGS

29 Figure 1 is a schematic illustration of a two-stage
30 primary/secondary reforming process of the prior art.

31 Figures 2 and 3 are a schematic illustration of one
32 embodiment of the process of the present invention.

33 Figure 4 is a schematic illustration of a
34 reactor/exchanger for use in a second embodiment of the
35 process of this invention.

36

DETAILED DESCRIPTION OF THE INVENTION

37

Referring to the drawings, and specifically the

1 conventional primary and secondary reforming stages which
2 have been highly simplified and illustrated in Figure 1,
3 there is seen a primary reforming furnace stage generally
4 indicated by the numeral 10, having an upper convection
5 section 8, and a lower primary reforming radiant section 12.
6 The furnace is normally heated by burners mounted in the
7 floor of the radiant section and supplied with fuel gas and
8 combustion air as illustrated. Hot flue gas exiting the
9 radiant section flows upwardly through convection section 8,
10 past steam superheat exchangers 4 and 6, process air heat
11 exchanger 7, steam generators 9 and 11, steam superheat
12 generator 13, feed gas heat exchangers 15, and 16 and
13 boiler feed water preheater 17, and is discharged through
14 port 3.

16 As discussed previously, conventional two-stage
17 reforming processes require the introduction of four separate
18 process streams to the primary reformer: feed gas (for a
19 source of hydrogen), steam, a source of nitrogen gas (which
20 is conventionally process air) and fuel gas. Feed gas is
21 introduced into the process and passes through feed gas heat
22 exchangers 16 and 15, positioned in the primary reforming
23 furnace's convection section 8.

24 This preheats the feed gas to approximately 750°F, the
25 required temperature for the removal of sulfur over a zinc
26 oxide desulfurization bed 20. Steam is produced by passing
27 boiler feed water through heat exchangers 17, 9, and 11, and
28 by passing the resulting steam for superheating through
29 exchangers 13, 6 and 4, via steam drum 18, as shown, to
30 achieve a steam temperature of approximately 1200°F. This
31 steam is then combined with the desulfurized feed gas and fed
32 to catalyst-filled reformer tubes 14 in radiant section 12.
33 The partially reformed feed gas 28 is then discharged from
34 the primary reformer furnace and fed into secondary adiabatic
35 reformer 30 where it is combined with process air 29 that has
36 been preheated in heat exchanger 7 to about 1200°F. The
37 oxygen in this preheated process air reacts with combustibles
38 (H_2 , CO, and CH_4) in the partially reformed feed gas, and
39 releases additional heat. Upon entering the secondary

1 reformer's catalyst bed the gas mixture undergoes additional
2 reforming with a decrease in temperature due to the more
3 predominant endothermic reaction. The raw synthesis gas is
4 discharged from the secondary reformer and undergoes addi-
5 tional processing in conventional steps: carbon dioxide is
6 formed from carbon monoxide in shift converter unit 40;
7 carbon dioxide is removed in process unit 50; carbon monoxide
8 and additional carbon dioxide is removed by methanation in
9 process unit 60; the synthesis gas is compressed in com-
10 pressor 70 to that required for ammonia synthesis in the
11 ammonia synthesis system 80; vaporous ammonia undergoes
12 further compression in refrigeration compressor 90; and is
13 withdrawn from the process as ammonia product. Excess heat in
14 the ammonia synthesis section is removed by means of boiler
15 feed water heat exchanger 82.

16 Referring to Figure 2, wherein one embodiment of the
17 process of this invention is illustrated, the selected
18 high-hydrogen content feedstock is passed via conduit 108 to
19 first heat exchanger 110 wherein it is heated, generally to a
20 temperature of from about 300 to 350°F, by indirect heat
21 exchange with a low temperature shift converter effluent gas,
22 to be described in more detail below, which is passed to
23 exchanger 110 via conduit 201.

24 The gas feedstocks which can be treated in accordance
25 with the process of this invention for single-stage reforming
26 are gases containing high concentrations of hydrogen, i.e.,
27 hydrogen concentrations greater than about 40 vol.%, and
28 preferably greater than about 50 vol.% H₂, and most typically
29 from about 50 to 80 vol.% H₂, in addition to lower hydro-
30 carbons, small concentrations of carbon monoxide, and trace
31 gases, such as CO₂, H₂S, COS, N₂ and argon. The lower
32 hydrocarbons present in the gas feed generally comprise
33 members selected from the group consisting of saturated
34 aliphatic hydrocarbons having from 1 to 4 carbon atoms, and
35 unsaturated aliphatic hydrocarbons having from 2 to 4 carbon
36 atoms; are principally methane but also inclusive of
37 ethylene, ethane and the like; and are generally present in a
38 concentration of from about 15 to 30 vol.%. The carbon

1 monoxide concentration in the gas feed is not critical and
2 will generally range from about 0 to 25 vol.%. Among these
3 potential high-hydrogen content feedstocks are coke gas or
4 refinery gases, such as are discussed in U.S. Patent
5 3,649,558, in addition to coal pyrolysis gas, and feedstocks
6 such as those available from an intermediate BTU gas (IBG)
7 streams resulting from the gasification of coal or lignite
8 using conventional gasification processes.

9 The heated feed gas is withdrawn from exchanger 110 via
10 conduit 112 and may be admixed with sufficient steam (which
11 can be introduced to conduit 112 via conduit 111) to supply
12 the water of reaction required for a subsequent COS hydroly-
13 sis reaction (which can be effected in COS hydrolysis reactor
14 114), if COS is present in the feed. The quantity of steam
15 which is thus introduced can vary widely and will generally
16 comprise from about 2 to 4 vol.%, based on the total feed
17 gas in conduit 112 withdrawn from exchanger 110. The COS
18 reaction in reactor 114 can be effected by any conventional
19 means, using conventional hydrolysis catalysts such as
20 activated alumina. In this reactor, COS contained in the feed
21 gas is converted into hydrogen sulfide gas at conventional
22 hydrolysis conditions, which typically range from about 300
23 to 350°F and from about 300 to 600 psig. If the feedstock
24 gas does not contain COS, steam injection line 111 and COS
25 hydrolysis reactor 114 can be eliminated from the system if
26 desired.

27 The resulting gas mixture is withdrawn via conduit
28 116 and is introduced into second heat exchanger 118 wherein
29 the gas is further heated, in this case by indirect heat
30 exchange with a high temperature shift converter gas effluent
31 (to be described in more detail below), which is introduced
32 thereto via conduit 164. Thereafter, the further-heated gas
33 which may contain the hydrogen sulfide and which will
34 generally have a temperature of from about 700 to 750°F, is
35 withdrawn via conduit 117 and introduced into sulfur removal
36 zone 120, wherein the hydrogen sulfide impurities are removed
37 from the gas stream by conventional technology, such as by
38 use of a zinc oxide adsorption bed. The gas, now essentially

1 free of sulfur impurities (e.g., containing less than about
2 0.2 ppm by weight of sulfur compounds, calculated as elemen-
3 tal sulfur), is withdrawn via conduit 122 and admixed with
4 steam, which can be accomplished by injected steam into
5 conduit 122 via conduit 124. Again, the quantity of steam
6 introduced at this point can vary, and will generally range
7 from about 2.5 to 4.0 moles per mole of carbon in the
8 desulfurized gas feed. The function of the steam introduced
9 at this point in the process is to provide the water of
10 reaction necessary for the subsequent reforming reactions.
11 The steam/desulfurized gas mixture is then further heated
12 (generally to a temperature of from about 800 to 1,000°F) in
13 third heat exchanger 126 by indirect heat exchanger with a
14 portion of the reactor/exchanger effluent gas (to be des-
15 cribed in more detail below) which is introduced to exchanger
16 126 via conduit 138. The thus-heated steam/desulfurized gas
17 mixture 128 is introduced into the tube side of tubular heat
18 exchanger 130 wherein the feed gas is at least partially
19 reformed by contacting the feed gas, under reforming condi-
20 tions, in tubes 121 of reactor/exchanger 130 with a conven-
21 tional reforming catalyst. Any conventional primary
22 reforming catalyst can be employed, such as nickel, nickel
23 oxide, chromia, molybdenum, mixtures thereof and the like,
24 with nickel-on-calcium aluminate or nickel-on-alumina being
25 preferred. The temperature within tubes 121 will generally
26 range from about 900 to 1500°F and the pressure will gener-
27 ally range from about 300 to 1000 psig, and the total gas
28 hourly space velocity in tubes 121 will generally range from
29 about 5000 to 15,000 v/v/hr., with a range of from 8000 to
30 10,000 v/v/hr. being preferred.

31 As a result of the reforming reactions occurring in
32 tubular exchanger 130, substantially all of the hydrocarbon
33 components of the feed gas (other than methane) are converted
34 to CH₄, CO, CO₂ and H₂; a portion of the original methane
35 components are likewise converted to CO, CO₂ and H₂; and the
36 temperature of the gas mixture will be generally increased to
37 about 1300 to 1450°F. The partially reformed gas will

1 generally have a residual methane level of from about 5 to
2 20 vol.% CH₄, on a dry basis.

3 Process air obtained from any convenient source is
4 passed via conduit 197 to fourth heat exchanger 196 wherein
5 it is heated (generally to a temperature of from about 700 to
6 800°F) by indirect heat exchange with a portion of the high
7 temperature shift converter effluent gas which is passed
8 thereto via conduit 166. The thus-heated process air is
9 withdrawn via conduit 195 and passed to yet another heat
10 exchanger 194 for further heating (generally to a temperature
11 of from about 900 to 1000°F) by indirect heat exchange with a
12 portion of the cooled reformer effluent gas, which is passed
13 thereto via conduit 135 from the shell side of exchanger 130.
14 The thus-heated process air is then introduced via conduit
15 141 into secondary reformer 140, together with the partially
16 reformed gas mixture which is introduced via conduit 136.

17 The quantity of air introduced via conduit 141 is
18 adjusted using conventional control means (not shown), to
19 provide an air:feed ratio sufficient to yield about a 3:1
20 hydrogen:nitrogen ratio in the ammonia synthesis gas, that
21 is, to provide a H₂:N₂ ratio of from about 2.6:1 to 3.2:1,
22 and preferably from about 2.8:1 to 3.1:1.

23 Secondary reformer 140 comprises an adiabatic reformer
24 of conventional design and can be provided with suitable
25 internal burners to be used during start-up of the process in
26 order to bring the temperature within the reformer to within
27 the range of from about 1400 to 1600°F, after which further
28 heating can be accomplished via the heat released in the
29 exothermic reaction of oxygen therein with feedstock. The
30 amount and type of catalyst in reformer 140 is also con-
31 ventional, with Ni catalysts supported on alumina being
32 typical. The secondary reformer will generally employ a
33 temperature of from about 1600 to 1900°F, a pressure of from
34 about 300 to 1000 psig, and a total gas hourly space velocity
35 of from about 7000 to 10,000 v/v/hr.

36 The reformer effluent gas (generally having a tem-
37 perature of from about 1600 to 1800°F and a residual CH₄
38 level of from about 0.2 to 0.6 vol.% CH₄, on a dry basis) is

1 withdrawn from secondary reformer 140 via conduit 134 and is
2 passed to the shell side of reactor/exchanger 130 for
3 indirect heat exchange with, and heating of, the
4 steam/desulfurized feed gas mixture passed to exchanger 130
5 via conduit 128, as described above. The effluent gas
5 withdrawn via conduit 132 is then divided into two portions.
7 A first portion is passed via conduit 138 to third heat
8 exchanger 126 for indirect heat exchange with, and heating
9 of, the steam/desulfurized gas mixture as described above.
10 The second portion is passed via conduit 135 to fifth
11 exchanger 194 to provide the final stage of heating of the
12 process air in conduit 195 prior to its injection into
13 secondary reformer 140. The partially cooled reformer
14 effluent gas is withdrawn from third exchanger 126 via
15 conduit 139 and passed to steam superheater 142 and first
16 steam generator 158, superheater 142 receiving steam via
17 conduit 144 (generally at a temperature of from about 590 to
18 600°F and about 1500 psig) from steam drum 150 and producing
19 superheated steam which is withdrawn via conduit 143
20 (generally at a temperature of about 800 to 900°F and about
21 1500 psig), and generator 158 in turn generating steam 159
22 from water stream 157 which is fed thereto from steam drum
23 150. From generator 158, the cooled reformer effluent is
24 passed via conduit 155 to high temperature shift converter
25 160, wherein carbon monoxide in the reformer effluent gas is
26 converted over conventional catalysts and using conventional
27 methods and equipment to carbon dioxide and additional
28 hydrogen. Partially cooled effluent gas is also withdrawn
29 via conduit 137 from fifth exchanger 194 and is recombined
30 with the remaining reformer effluent in conduit 155.
31 Generally, a temperature of from about 700 to 900°F and
32 a pressure of from about 300 to 1000 psig will be employed in
33 converter 160, and the catalyst will generally comprise a
34 supported, chromium-promoted iron catalyst. Thereafter, gas
35 exiting the high temperature shift converter is withdrawn via
36 conduit 162 and is itself split into two portions. A first
37 portion is passed via conduit 164 to second heat exchanger
38 118 for heating of the gas feed to desulfurization zone 120,

- 11 -

1 as described above. The partially cooled effluent gas is
2 then withdrawn via conduit 165 from exchanger 118 and passed
3 to low temperature shift converter 200, preferably after
4 treatment in guard bed 190.

5 The second portion of the gaseous effluent from the
6 high temperature shift converter 160 is passed via conduit
7 169 to a second steam generator 152 in which steam 151 is
8 produced from water feed 153 and is returned to drum 150 from
9 which water 153 was received. The partially cooled high
10 temperature shift effluent from generator 152 is then itself
11 split into two portions: a first part is passed via conduit
12 166 to fourth heat exchanger 196 to provide the first stage
13 of heating of the process air, introduced thereto via conduit
14 197, as described above. The further cooled effluent gas is
15 then withdrawn via conduit 167 and passed to conduit 165 for
16 combined feed to the low temperature shift converter 200, or
17 preferably first to guard bed 190.

18 The second part of shift effluent from exchanger 152 is
19 passed via conduit 168 to boiler feedwater exchanger 170 in
20 which boiler feedwater, introduced thereto via conduit 180,
21 is heated and from which the further cooled shift effluent is
22 withdrawn (via conduit 174) and combined with stream 165 for
23 feed to low temperature shift converter 200, or preferably
24 first to guard bed 190. If desired, feedwater 180 can be
25 first heated by exchange with low temperature shift effluent
26 201 in a separate exchanger (not shown) prior to introduction
27 to exchanger 170.

28 Guard bed 190, which is optional, is preferably
29 employed to treat gas stream 165 upstream of low temperature
30 shift converter 200 to remove halide and sulfur impurities
31 and thereby protect any halide- and sulfur-sensitive catalyst
32 in low temperature shift converter 200. The operation of
33 guard bed 190 is conventional and is generally conducted at
34 temperatures and pressures within the ranges used in low
35 temperature shift converter 200 as described below, and the
36 solids employed in guard bed 190 for such halide- and
37 S-impurities removal generally comprise the same catalyst as
38 is used in low temperature shift converter 200.

1 In shift converter 200, a low temperature shift
2 conversion reaction is effected over conventional catalyst
3 using conventional methods and equipment to form additional
4 quantities of H_2 and CO_2 . Generally, a temperature of from
5 about 400 to 500°F and a pressure of from about 300 to 1000
6 psig will be employed in converter 200, and the catalyst will
7 generally comprise a mixture of zinc oxide and copper. The
8 effluent gas from low temperature shift converter 200 is
9 passed via conduit 201 to first heat exchanger 110, as
10 described above, for heating of the feed gas introduced
11 thereto via conduit 108. The cooled, low temperature shift
12 converter effluent gas, now depleted of its heat values, is
13 then withdrawn via conduit 106 and (referring now to Figure
14 3) can be passed to CO_2 -removal zone 250, in which any
15 conventional process (e.g., solvent absorption of CO_2 gas)
16 can be used to remove CO_2 via conduit 210. The resulting
17 CO_2 -free gas is fed by conduit 220 to conventional methana-
18 tor zone 300 for removal of additional CO and CO_2 and is then
19 withdrawn (via conduit 320), compressed in compressor 350 and
20 passed as direct feed via conduit 370 to ammonia synthesis
21 zone 400, wherein NH_3 is formed from the H_2/N_2 synthe-
22 sis gas 370 (i.e., 3:1 $H_2:N_2$ molar ratio) using conven-
23 tional techniques (i.e., over Fe-catalyst at 700 to 950°F).
24 Waste gases are withdrawn via conduit 410 and product NH_3 is
25 recovered via conduit 420.

26 The operation of CO_2 removal zone 250, methanation zone
27 300, compressor 350 and NH_3 synthesis zone 400 is conven-
28 tional and need not be more completely described for a full
29 understanding of the process of this invention. The precise
30 operating parameters and equipment of each such process step,
31 therefore, will be readily apparent to one having ordinary
32 skill in the art, and each step can include the usual
33 internal recycle streams and stages found useful in the prior
34 art. Thus, CO_2 -removal zone 250 can include conventional
35 CO_2 -absorption and CO_2 -desorption stages wherein the
36 CO_2 -laden gas 106 is contacted with a liquid containing
37 either a solvent for, or a dissolved compound (e.g., K_2CO_3)
38 readily reactive with, the CO_2 ; the CO_2 -free gases (generally

1 containing less than about 0.15 vol.% CO₂) are withdrawn; and
2 the solvent is treated to desorb the CO₂ gases 210 for
3 recycle of solvent to the absorber. Exemplary of suitable
4 conventional CO₂ removal systems are those discussed in
5 Kirk-Othmer, Encyclopedia of Chemical Technology, 3d Ed.,
6 Vol. 2, pp. 492-494 (1978). Similarly, methanator 300 will
7 generally employ a temperature in the range of about 570 to
8 940°F, a pressure from about 300 to 1000 psig, and a sup-
9 ported Ni catalyst (e.g., Ni on alumina) to convert any
10 remaining CO and CO₂ in gas stream 220 to methane, thereby
11 producing an effluent gas 320 containing less than about 10
12 vppm (i.e., parts per million by volume) of total CO and CO₂
13 and H₂ and N₂ in a H₂:N₂ molar ratio of from about 2.6:1 to
14 3.1:1. Compression in zone 350 can take place in several
15 stages, as desired, to bring the methanator effluent to
16 synthesis reactor pressure, which generally ranges from about
17 2000 to 5000 psig. Finally, ammonia synthesis zone 400 can
18 include conventional dryer units wherein trace water is
19 removed from the syn gas as required and conventional purge
20 recovery units wherein a portion or all of the gas effluent
21 from the ammonia synthesis reactor is treated to recover and
22 recycle H₂ to the reactor and to remove inerts such as CH₄
23 and Ar therefrom.

24 The improved process of this invention produces a syn
25 gas 370, having a H₂:N₂ molar ratio of about 3:1, that is a
26 H₂:N₂ molar ratio of from about 2.6:1 to 3.2:1, and which has
27 a residual methane concentration (dry basis) of less than
28 about 2 vol.%, and more typically less than about 1 vol.% and
29 which is therefore suitable for direct feed to an ammonia
30 synthesis reactor zone 400, that is a syn gas 320 which is
31 not subjected to a cryogenic purification following methana-
32 tor 300 to remove excess methane prior to the ammonia
33 synthesis reaction. The elimination of the cryogenic section
34 required by the prior art and the avoidance of the use of a
35 primary reformer furnace by the improved process of this
36 invention results in a very large savings in terms of
37 equipment investment and operating expense.

38 In accordance with another embodiment of the process of
39 this invention, illustrated in Figure 4, steam/desulfurized

1 gas mixture 128a is passed to the shell side of reactor/
2 exchanger 130a and the selected reforming catalyst is
3 housed in the shell side of apparatus 130a. The steam/
4 desulfurized gas mixture is at least partially reformed
5 over the catalyst while being heated by means of reformer
6 effluent gas 134a, which in this embodiment is passed to the
7 tube side 121a of reactor/exchanger 130a. The partially
8 reformed gas 136a and the partially cooled reformer effluent
9 gas 132a are withdrawn and further treated as described above
10 for streams 132 and 136, respectively, in the embodiment
11 illustrated in Figure 2. The conditions of operation of
12 apparatus 130a in Figure 4 correspond to those discussed
13 above for apparatus 130 in the embodiment illustrated in
14 Figure 2.

15 To further illustrate the process, a feed gas con-
16 taining 52 vol.% H₂, 20 vol.% CO, 28 vol.% CH₄ and 30 vppm
17 COS, having a temperature of about 110°F and a pressure of
18 about 350 psig, is preheated to about 315°F in tubular feed
19 gas preheat exchanger 110, and is then introduced into COS
20 hydrolysis drum 114, after addition of 2 vol.% steam (750°F,
21 600 psig), based on total feed gas 112, (withdrawn from
22 exchanger 110), in which the carbonyl sulfide is converted to
23 hydrogen sulfide over a bed of an alumina hydrolysis catalyst
24 (at 315°F, 350 psig, 2000 v/v/hr. gas hourly space velocity).
25 The temperature of the resulting feed gas is increased to
26 about 750°F, the temperature required for further desulfur-
27 ization, by passing the hydrogen-sulfide-containing gas
28 through tubular heat exchanger 118, followed by adsorption of
29 the hydrogen sulfide over a zinc oxide adsorption bed 120.

30 To the sulfur-free feed gas discharged from zinc oxide
31 adsorption bed 120 is then added 3.0 moles of steam (750°F,
32 600 psig) per mole of carbon in the feed gas, and this
33 combined stream passes through tubular heat exchanger 126 in
34 order to increase the gas temperature to about 900°F.

35 An additional increase in the temperature of this
36 combined stream (to about 1400°F) is obtained by subsequent
37 preheat treatment in the tube side 121 of reactor/exchanger
38 130 in indirect heat exchange with reformer effluent gas

1 entering the shell side of exchanger 130 and in contact with
2 nickel on alumina reforming catalyst in tubes 121 (at 1375°F,
3 325 psig, 9000 v/v/hr.) so that partial steam reforming of
4 hydrocarbons takes place in exchanger 130, further con-
5 tributing to the preheat of this feed stream to be charged to
6 reformer 140.

7 Process air is adjusted using conventional control
8 means (not shown) to provide an air:feed ratio sufficient to
9 yield about a 3:1 H₂:N₂ ratio in the final product ammonia
10 synthesis gas 320. The adjusted process air enters the
11 process by first being pressurized (compressor not shown) to
12 about 50 psi above the pressure used in reformer 140. The
13 pressurized process air is then preheated in tubular heat
14 exchangers 196 and 194 to a reforming inlet temperature of
15 about 1000°F.

16 The heated process air feed and the steam-feed gas
17 streams are then introduced into adiabatic reformer 140
18 wherein reforming of the feed gas takes place over Ni on
19 alumina reforming catalyst (at a space velocity of about 7000
20 v/v/hr.).

21 The reformer effluent gas from reformer 140 (1730°F,
22 320 psig) is discharged, as discussed above, into the shell
23 side of exchanger 130, and from exchanger 130 (1130°F, 315
24 psig) is passed to feed preheat exchanger 126 and air preheat
25 exchanger 194. The partially cooled reformer effluent from
26 feed gas preheat exchanger 126 is passed to steam superheater
27 142 and first steam generator 158 for generation of 1500 psig
28 steam, and the resulting cooled reformer effluent withdrawn
29 from generator 158 is combined with the remaining cooled
30 reformer effluent 137 and passed via conduit 155 (700°F, 310
31 psig) to high temperature shift converter 160. In converter
32 160, a water gas shift reaction is effected over an
33 iron-based catalyst (720°F inlet temperature, 310 psig) to
34 form H₂ and CO₂ from CO contained in the reformer effluent
35 gas. Gases exiting converter 160 (850°F, 300 psig) are then
36 passed to heat exchangers 118, 196 and 170 and steam
37 generator 152 (generating steam at 1500 psig) as described
38 above, combined in conduit 165 (420°F, 300 psig) and fed to

1 low temperature converter guard bed 190 containing ZnO/Cu
2 solids to absorb any Cl and S values which may be present,
3 followed by treatment in low temperature shift converter 200
4 containing conventional ZnO/Cu shift conversion catalyst.
5 After passing through heat exchanger 110, the product gases
6 (at 450°F, 290 psig) are withdrawn via conduit 106, and
7 treated for CO₂ removal in CO₂ removal zone 250, methanated
8 in methanator 300, compressed and then fed to ammonia
9 synthesis zone 400, as described above. The ammonia synthesis
10 gas withdrawn from methanator 300 contains H₂:N₂ in about a
11 3:1 molar ratio and contains less than about 1.0 vol.% CH₄
12 (dry basis), and less than about 10 vppm CO and CO₂.

13 A feedstock 108 suitable for the single stage reforming
14 process of the present invention is, for example, a steam
15 cracker tail gas having a hydrogen content of about 70%, with
16 the remainder being methane, or an IBG stream from a coal
17 gasification process having major component composition of
18 hydrogen (60%), carbon monoxide (20%), and methane (16%).
19 Still another feedstock suitable for the single stage
20 reforming process of the present invention, and that used as
21 the feedstock material for obtaining the data in Table 1 has
22 the composition of hydrogen (52.13%), carbon monoxide
23 (19.39%), methane (27.03%), carbon dioxide (0%), nitrogen
24 (0%), and mixed 2-carbon hydrocarbons (1.45%).

25 A comparison of the parameters is tabulated in the
26 following Table 1 for (1) a conventional process as shown in
27 Figure 1, except that the primary reformer is omitted,
28 conducted at the maximum practical preheat temperature for
29 feedstock and air; and (2) single stage reforming using the
30 feed/effluent reactor/exchanger 130, as depicted in Figure
31 2.

TABLE 1
SINGLE-STAGE REFORMING OF
IBC FOR AMMONIA SYNTHESIS GAS

	Maximum Feed Preheat-Conventional (without Primary Reforming)	Apparatus/Stream No. (Fig. 1*) (1)	Reactor/ Exchanger (Figures 2&3)	Apparatus/Stream No. (Figures 2&3)
Feed/Steam Preheat Temperature, °F	916	28	900	128
Air Preheat Temperature, °F	1000	29	1000	141
Steam/Feed, mols/mol	1.479	28	1.479	128
Reformer Pressure, psia	350	30	335	140
Vol.% O ₂ in Air Stream	20.95	29	20.95	141
Reformer Feed/Steam Inlet Temperature, °F	916	28	1375	128
Reformer Outlet Temperature, °F	1413	32	1732	134
Vol.% CH ₄ in Reformer Outlet (dry basis)	5.86	32	0.34	134
Vol.% CH ₄ in Syn Gas Product (dry basis)	7.04	66	0.92	320
Feed Gas/Product H ₂ , mols/mol	0.88	66	0.65	320

1 Figure 1* = process of Figure 1 without reforming in primary reformer 10; composition of feed gas/steam mixture 24 is the same as stream 28 which is passed directly to secondary reformer 30.

1 Table 1 clearly indicates that a feed/steam preheat to
2 1375°F in the reactor/exchanger and accompanying partial
3 reforming of hydrocarbons therein results in a decrease in a
4 final product syn gas methane content from an unacceptably
5 high 5.86 vol.% to 0.34 vol.%, thereby indicating the greater
6 reforming efficiency obtained utilizing the reactor/exchanger
7 130.

8 When the amount of feed gas required to produce a
9 constant amount of hydrogen in the ammonia syn gas is
10 calculated, the efficiency of the total process is easily
11 seen. For example, as shown in Table 1, 0.65 lb-mols/hr. of
12 feed gas are required to produce 1.0 lb-mols/hr. of hydrogen
13 in the product syn gas in the reactor/exchanger process
14 design depicted in Figure 2, whereas 0.88 lb-mols/hr. of feed
15 gas are required to produce the same amount of hydrogen under
16 the conventional process design depicted in Figure 1 when the
17 primary reformer is omitted.

18 The advantages of the process design according to the
19 present invention are therefore seen as a reduction in
20 capital expenditure associated with the construction of a
21 primary reforming furnace, as otherwise required to produce
22 an acceptable concentration of methane in product synthesis
23 gas, an economic savings in utility costs expended in the
24 heating of said primary reforming furnace, a desirable
25 decrease in the methane slippage of the ammonia syn gas
26 produced, and a greater efficiency in utilizing the feed gas
27 requirements to yield the ammonia syn gas produced.

28 Thus, while I have illustrated and described the
29 preferred embodiment of my invention, and have described my
30 invention and the manner and process of making and using it
31 in such full, clear, concise and exact terms as to enable any
32 person skilled in the art to which it pertains to make and
33 use the same, one skilled in the art can easily ascertain the
34 essential characteristics of this invention and without
35 departing from the spirit and scope thereof can make various
36 changes and/or modifications to the invention for adapting it
37 to various usages and conditions. Accordingly, such changes
38 and/or modifications are properly intended to be within the
39 full range of equivalents of the following claims.

CLAIMS:

1. In a process for producing an ammonia synthesis gas from a methane-containing feedstock gas which includes the steps of reforming the methane-containing feedstock gas in the presence of steam, treating the reformed gas in a shift conversion zone to convert CO catalytically with steam to CO₂ and hydrogen; and removing CO and CO₂ by absorption and methanation from the gas stream withdrawn from the shift conversion zone, the improvement which comprises employing as said feedstock gas a desulfurized, hydrogen-rich gas containing methane and

- (a) reforming said hydrogen-rich gas by the steps of:
 - (i) admixing steam with said hydrogen-rich gas and partially reforming the resulting gas mixture in a tubular heat exchanger containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas; and
 - (ii) recovering a partially reformed gas product from said tubular heat exchanger and secondarily reforming said recovered, partially reformed gas product in a secondary reformer in the presence of air, said air being introduced to said secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3:1 in the ammonia synthesis gas;
- (b) recovering a secondary reformer gas effluent from said secondary reformer and passing said secondary reformer effluent to said tubular heat exchanger for indirect heating of said hydrogen-rich feedstock and steam gas mixture; and

(c) recovering a partially cooled, secondary reformer effluent from said tubular heat exchanger and passing said partially cooled effluent as feed to said shift conversion zone, whereby said ammonia synthesis gas is withdrawn from said methanation step and is suitable for direct feed to an ammonia synthesis reaction.

2. The process of claim 1 wherein said desulfurized, hydrogen-rich feedstock gas contains hydrogen in a concentration of at least about 40 vol.%.

3. The process of claim 2 wherein said desulfurized hydrogen-rich feedstock gas contains methane in a concentration of from about 10 to 50 vol.%, calculated on a dry basis.

4. The process of claim 1 wherein said desulfurized hydrogen-rich feedstock gas contains hydrogen in a concentration of from about 50 to about 80 vol.% and contains methane in a concentration of from about 16 to about 40 vol.%, calculated on a dry basis.

5. The process of claim 1 wherein said desulfurized hydrogen-rich feedstock gas is obtained by subjecting a hydrogen-rich gas containing COS to hydrolysis in a hydrolysis zone in the presence of steam to form H₂S from said COS, and removing said H₂S to form said desulfurized feedstock gas.

6. A process for the production of an ammonia synthesis gas which comprises

(a) forming a mixture comprising steam and desulfurized hydrogen-rich feedstock gas having a temperature of from about 800 to 1200°F;

- (b) passing said steam/feedstock gas mixture to a tubular heat exchanger containing reforming catalyst for partial steam reforming of said feedstock gas, while maintaining said steam/feedstock gas mixture in indirect heat exchange with a secondary reformer effluent gas;
- (c) passing said partially reformed gas mixture and process air, having a temperature of from about 800 to 1200°F, as feeds to said secondary reformer for secondary reforming of said partially reformed feedstock gas;
- (d) withdrawing a gaseous effluent from said secondary reformer and passing said secondary reformer effluent gas to said tubular heat exchanger for said indirect heating of said steam/feedstock gas mixture;
- (e) withdrawing a partially cooled reformer effluent from said tubular heat exchanger and employing said partially cooled reformer effluent to heat additional quantities of said steam/feedstock gas mixture and said process air, thereby forming a further cooled secondary reformer effluent gas having a temperature of from about 1000 to 1200°F;
- (f) passing said further-cooled secondary reformer effluent gas to a shift converter zone wherein shift conversion reactions are effected; and
- (g) recovering an effluent gas from said shift converter zone and treating said shift converter effluent by solvent absorption and methanation to remove CO and CO₂, to form an ammonia synthesis gas which is suitable as direct feed to an ammonia synthesis reaction.

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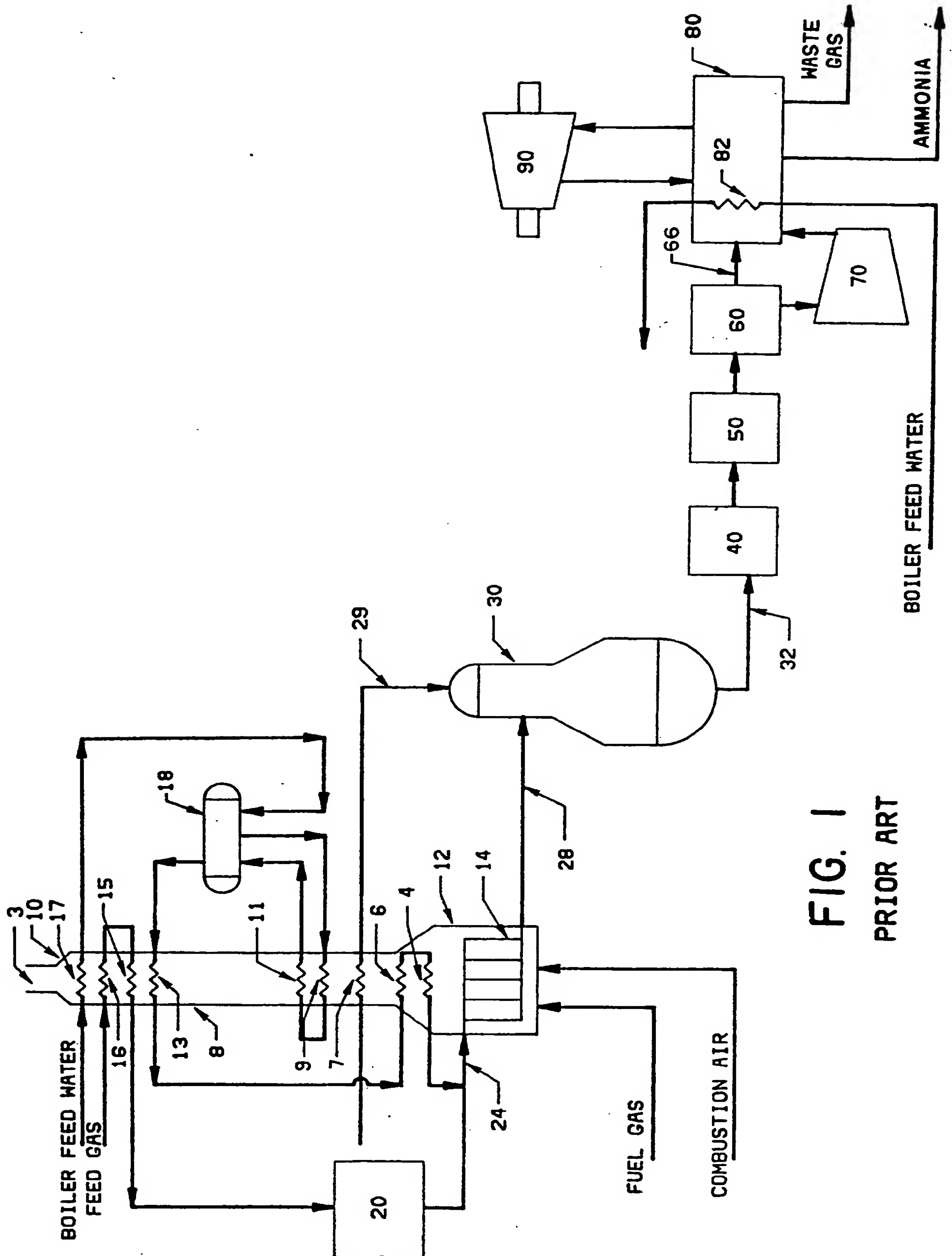


FIG. 1
PRIOR ART

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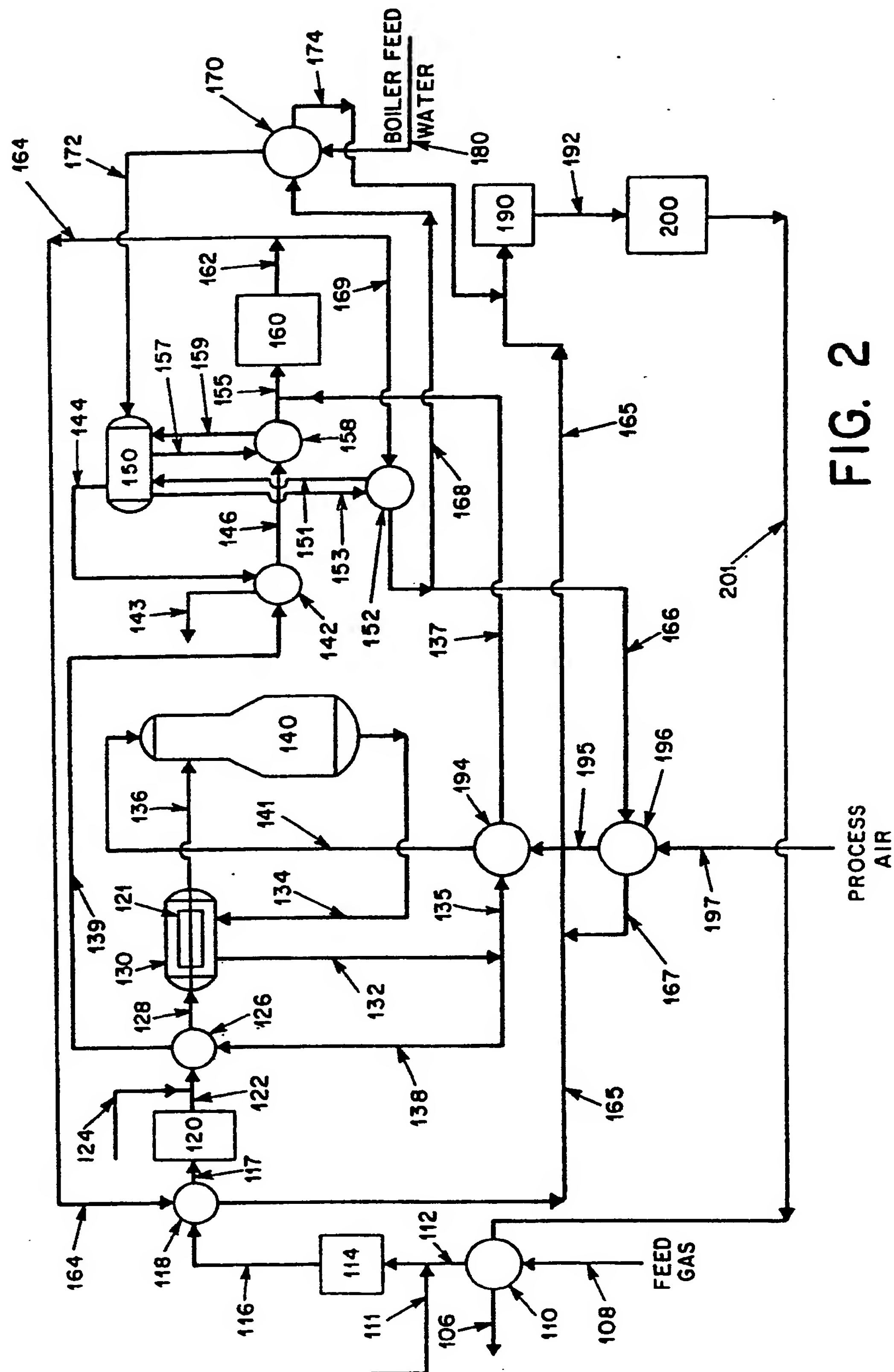


FIG. 2

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FIG. 3

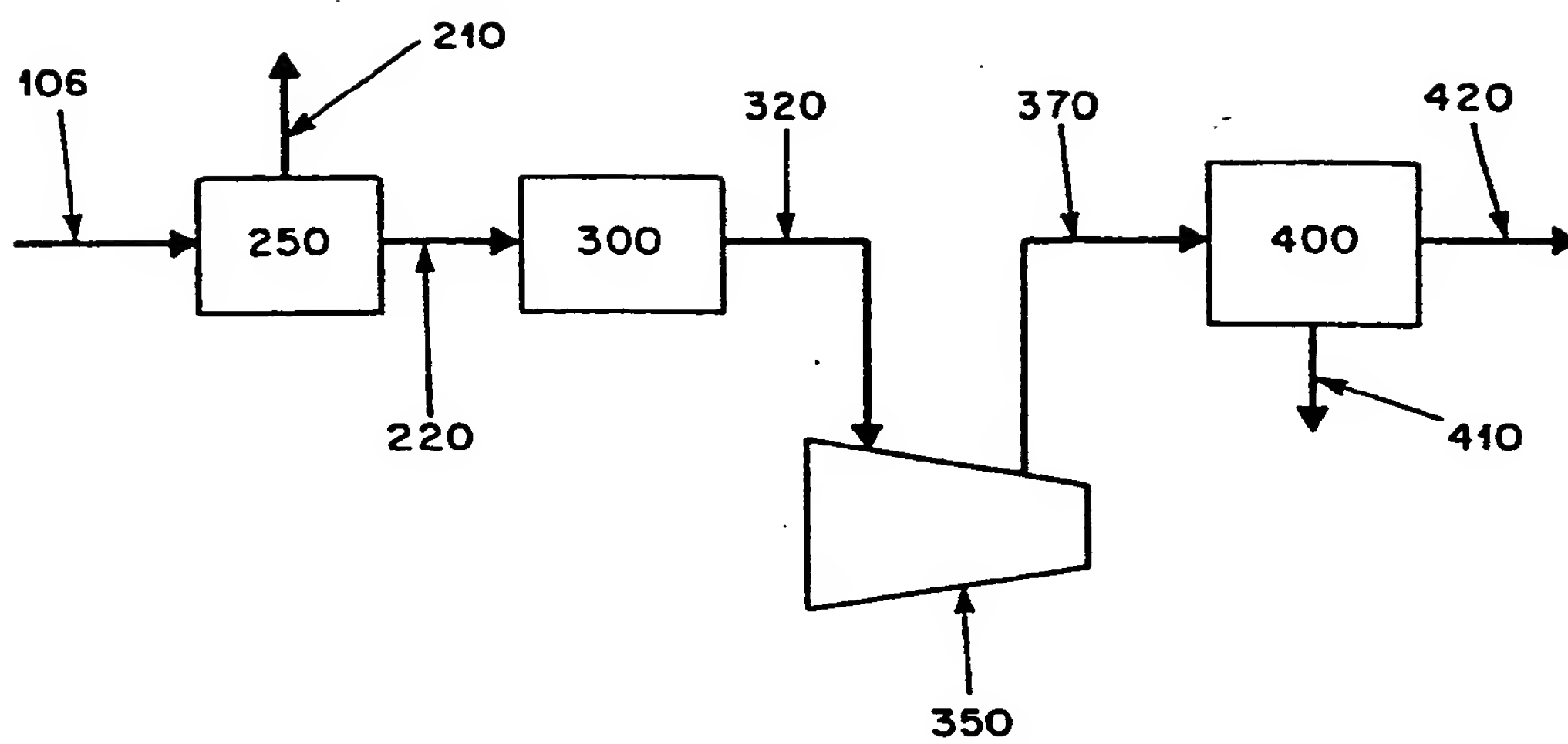
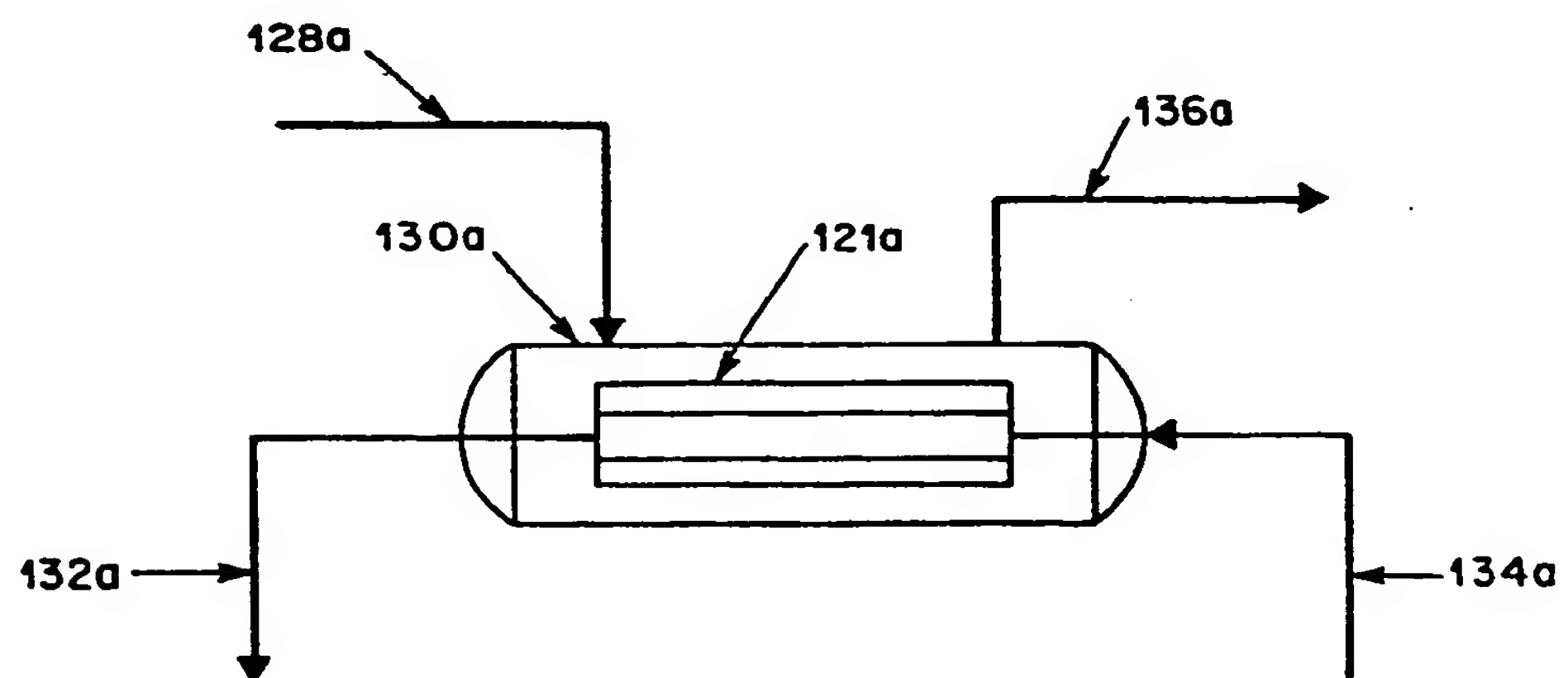


FIG. 4



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54 Single-stage reforming of high hydrogen content feeds for production of ammonia syn gas.

57 Process for the production of ammonia synthesis gas by steam reforming a desulfurized high-hydrogen-content feedstock gas (122) by admixing steam (124) therewith and partially reforming the resulting gas mixture in a tubular heat exchanger (130) containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas (134); recovering a partially reformed gas product (136) from the tubular heat exchanger and secondarily reforming this gas in a secondary reformer (140) in the presence of air, which is introduced to the secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3 : 1 in the ammonia synthesis gas; and treating the reformed gas (134) in a shift conversion zone (160 + 200) to convert CO catalytically with steam to CO₂ and hydrogen to form a gas which can be treated for removing CO and CO₂ by absorption and methanation to produce the ammonia synthesis gas.

ACTORUM AG



European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 83 30 7344

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-E- 24 311 (MADER) * claim 1 *	1	C 01 B 3/02
A,D	--- US-A-4 079 017 (CRAWFORD et al.) * claim 1 *	1	
A,D	--- US-A-3 584 998 (GREEN) * column 2, lines 32-35 *	1	
A	--- GB-A-2 067 175 (MONTEDISON S.P.A.) * claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 01 B 3/02
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 02-12-1986	Examiner CLEMENT J.P.
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